Synthesis of LaMnO$_{3+\delta}$ by Firing Gels Using Citric Acid

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A gel was prepared by adding citric acid to an aqueous solution of lanthanum nitrate and manganese nitrate. From thermal analysis and IR measurement, the gel prepared with 0.0023 mol of citric acid is a mixture of LaMn(C$_6$H$_5$O$_7$)(NO$_3$)$_3$, La(NO$_3$)$_3 \cdot x$H$_2$O, and Mn(NO$_3$)$_2 \cdot x$H$_2$O; the gel with 0.007 mol of citric acid LaMn(C$_6$H$_5$O$_7$)(NO$_3$)$_3$; and the gel with 0.015 mol of citric acid is LaMn(C$_6$H$_5$O$_7$)$_2$. Hexagonal perovskite-type LaMnO$_{3+\delta}$ was obtained by firing the gels. The specific surface area, the La/Mn ratio, and the catalytic activity for CO oxidation on LaMnO$_{3+\delta}$ were measured. The catalytic activity for CO oxidation on LaMnO$_{3+\delta}$ synthesized using citric acid is better than that on LaMnO$_{3+\delta}$ synthesized using poly(acrylic acid). For these results, citric acid is inferred to improve the crystallinity (regularity of the ions) of the LaMnO$_{3+\delta}$ surface. © 1997 Academic Press

INTRODUCTION

Perovskite-type LaMO$_{3+\delta}$ (M = Cr, Mn, Fe, Co, and Ni) shows high catalytic activity for the oxidation of carbon monoxide (CO) or hydrocarbons (1–5). According to Seiyama, the catalytic activity for the oxidation of CO on LaNiO$_3$ is higher than it is on NiO (6). LaMO$_{3+\delta}$ is generally synthesized at high temperature using a solid-state reaction, so the specific surface area of LaMO$_{3+\delta}$ is less than 5 m^2/g (2, 3). To improve the catalytic activity, it is necessary to synthesize LaMO$_{3+\delta}$ with a large specific surface area.

Taguchi *et al.* reported that LaMnO$_{3+\delta}$ and LaCoO$_{3+\delta}$ with ≈ 20 m^2/g were easily synthesized using poly(acrylic acid) (PAA) at low temperature (7, 8). Recently, we noticed that the crystal structure and the oxygen content of LaMnO$_{3+\delta}$ are strongly influenced by the PAA concentration. Therefore, we synthesized LaMnO$_{3+\delta}$ using gels with various PAA concentrations at low temperature and examined the relationship among the PAA concentration, the crystal structure, and the oxygen content (9). PAA plays an important role in making a gel from the aqueous solution of lanthanum nitrate and manganese nitrate and provides the heat of combustion for the synthesis of LaMnO$_{3+\delta}$. The rapid combustion of PAA caused many cracks in LaMnO$_{3+\delta}$, resulting in a large specific surface area. From the results of catalytic activity and the amount of absorbed oxygen on (La$_{1-x}$Sr$_x$)MnO$_3$ synthesized using PAA and the solid-state reaction, the surface of the samples synthesized using PAA had insufficient crystallization and fewer adsorption sites in comparison with the samples synthesized using the solid-state reaction (10).

In the present study, we tried to use citric acid to make gels of lanthanum nitrate and manganese nitrate and determined the structural formula of the gels. Then we synthesized LaMnO$_{3+\delta}$ by firing the gels in air. The crystal structure, oxygen content, crystallite size, specific surface area, La/Mn ratio, and catalytic activity for CO oxidation on LaMnO$_{3+\delta}$ were measured. These results will provide some information about the synthesis of LaMnO$_{3+\delta}$ and the crystallinity of the LaMnO$_{3+\delta}$ surface.

EXPERIMENTAL

Powders of La(NO$_3$)$_3 \cdot$6H$_2$O and Mn(NO$_3$)$_2 \cdot$6H$_2$O were weighed in equimolar amounts (0.007 mol) and dissolved in a small amount of distilled water. Citric acid (0.0023, 0.006, 0.007, 0.008, 0.009, and 0.015 mol) was used to make a gel. Gelation was achieved by keeping the solution at 100°C for 12 hr. The gel was fired at 300–900°C for 6 hr in air. The heating rate was 10°C/min. For

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comparison, LaMnO$_{3+\delta}$ was also synthesized using PAA and the solid-state reaction (10).

Thermal analysis (DTA and TG) of the gels was performed at a heating rate of 10°C/min to determine the reaction temperature of the gel. Infrared absorption (IR) spectra of the gels were measured using the KBr method. The crystal phases of the samples were identified by X-ray powder diffraction using monochromatic Cu$K\alpha$ radiation. The oxygen content of the samples was determined by an oxidation–reduction (redox) method (11). The crystallite size (D_{024}) of the samples was calculated from the half-width of a diffraction peak (024) using Scherrer's equation (12). The XPS measurements for the La3d, Mn2p, O1s, and C1s levels of the samples were carried out using Mg$K\alpha$ radiation at room temperature. The binding energy was calibrated using the C1s level from the usual contamination. The specific surface area of the samples was determined by the BET method for nitrogen adsorption. The catalytic activities for the oxidation of CO were measured at 195–300°C using a conventional flow system. The samples (0.10 g) were preheated at 300°C in a pure oxygen stream for 3 hr. A mixed gas of CO (1.0%), O$_2$ (4.0%), and He (balance) was fed in a flow reactor at a flow rate of 150 cm$^3 \cdot$ min^{-1}. The products were analyzed by gas chromatography using a column (Molecular Sieve 5A) kept at 50°C during the measurements.

RESULTS AND DISCUSSION

Gel formation was possible in the molar range from 0.0023 to 0.015 mol of citric acid. A brown smoke that evolved from the nitrate ion was given out from the gels at 100°C, and the amount of the smoke increased with increasing amount of the citric acid. Figures 1a, 1b, and 1c show the results of thermal analysis (DTA and TG) of the gels with 0.0023, 0.007, and 0.015 mol of citric acid, respectively. In Fig. 1a, we observed small endothermic peaks (90, 130, 270, and 340 °C) and a large exothermic peak (160°C) on the DTA curve. The total weight loss below 500°C is $\approx 58\%$. In Fig. 1b, we observed both a small endothermic peak (80°C) and a large exthothermic peak (190°C) on the DTA curve. Abrupt weight loss was observed at 195°C, and the total weight loss below 500°C is $\approx 58\%$. In Fig. 1c, we observed
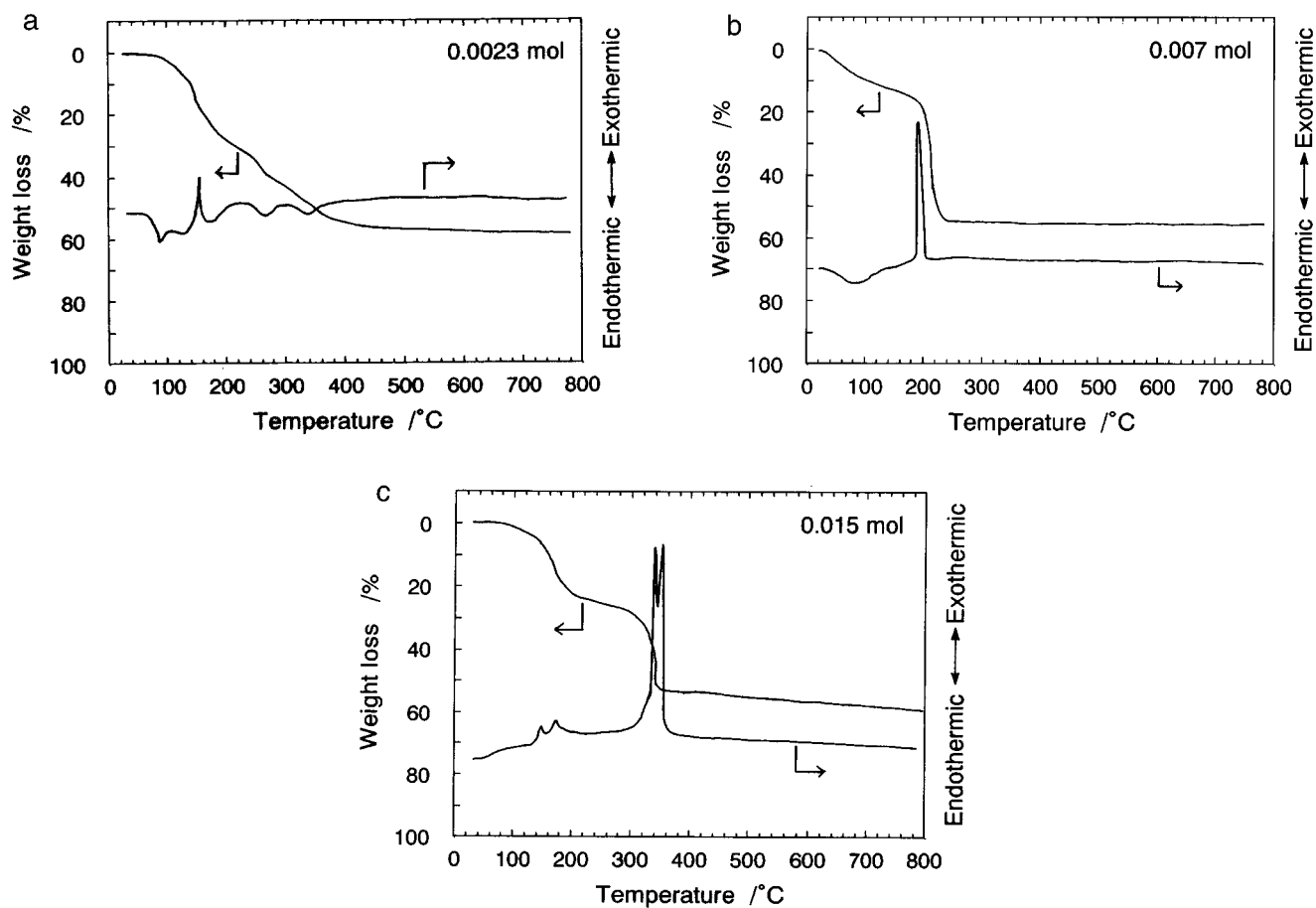

FIG. 1. Thermal analysis (DTA and TG) of the gels with 0.0023, 0.007, and 0.015 mol of citric acid.

small exthothermic peaks (150 and 170°C) and large exthothermic peaks (340 and 350°C). There are two steps in the TG curve, and total weight loss below 500°C is $\approx 57\%$. The exthothermic peak shifts to higher temperature with increasing amount of citric acid.

Figure 2 shows the IR spectra of the gels with 0.0023, 0.007, and 0.015 mol of citric acid. The absorption peaks or shoulders in Fig. 2 could be assigned to the methylene group (≈ 720 cm^{-1} for a rocking vibration and ≈ 1465 cm^{-1} for a scissoring band), the carboxylate anion (≈ 1550–1650 cm^{-1} for strong asymmetric stretching and ≈ 1400 cm^{-1} for weak symmetric stretching), and the nitrate ion (≈ 1440 and ≈ 820 cm^{-1} for NO stretching) (13, 14). The gels with 0.0023 and 0.007 mol of citric acid had the absorption peaks due to the nitrate ion. The gel with 0.015 mol of citric acid had sharp peaks due to the carboxylate anion, and the NO stretching was not observed.

From the results of thermal analysis and IR measurement, we determined the chemical composition of the gels. As for the gel with 0.0023 mol of citric acid, it is obvious that the gel lacks citric acid. The gel is considered to be a mixture of $LaMn(C_6H_5O_7)(NO_3)_3$, lanthanum nitrate, and manganese nitrate. The exothermic peak at 170°C and endothermic peaks correspond to the combustion of $LaMn(C_6H_5O_7)(NO_3)_3$ and the decomposition of nitrates. Since the amount of water of crystallization in lanthanum nitrate and manganese nitrate varies with temperature, they are defined as $La(NO_3)_3 \cdot xH_2O$ and $Mn(NO_3)_2 \cdot xH_2O$. Therefore, it is very difficult to calculate the theoretical weight loss of the gel with 0.0023 mol. As for the gel with 0.007 mol of citric acid, citric acid is equivalent with lanthanum nitrate and manganese nitrate, and brown smoke was given out from the gel. As the methylene group, carboxylate anion, and nitrate ion are detected in the IR

spectra, the gel is considered to be $LaMn(C_6H_5O_7)(NO_3)_3$. The molecular weights of $LaMn(C_6H_5O_7)(NO_3)_3$ and $LaMnO_3$ are 568.85 and 241.85, respectively. The theoretical weight loss is $\approx 57\%$ in the reaction $LaMn(C_6H_5O_7)(NO_3)_3 \rightarrow LaMnO_{3+\delta}$ and is nearly equal to the observed weight loss. As for the gel with 0.015 mol of citric acid, excess citric acid was added to make the gel, and the brown smoke was given out from the gel. The disappearance of the peaks at ≈ 1440 and ≈ 820 cm^{-1} indicates that the gel is $LaMn(C_6H_5O_7)_2$. The molecular weight of $LaMn(C_6H_5O_7)_2$ is 571.85. The theoretical weight loss is $\approx 58\%$ in the reaction $LaMn(C_6H_5O_7)_2 \rightarrow LaMnO_{3+\delta}$, and is nearly equal to the observed weight loss.

Figure 3 shows the relationship between the crystal structure of the samples and synthesis condition (the amount of citric acid and the firing temperature). Hexagonal $LaMnO_{3+\delta}$ was not obtained below 700°C by firing the gel with 0.006 mol of citric acid. Above 0.007 mol of citric acid, however, hexagonal $LaMnO_{3+\delta}$ was easily obtained by firing the gels at low temperature. The oxygen content $(3 + \delta)$ of $LaMnO_{3+\delta}$ is independent of the synthsis condition and is shown in Table 1. The crystallite size (D_{024}) of $LaMnO_{3+\delta}$ was calculated from the half-width of the diffraction peak (024) using Scherrer's equation (12). D_{024} is shown in Table 1, and has a minimum value at 0.007 mol of citric acid. The specific surface area of $LaMnO_{3+\delta}$ is also shown in Table 1, and has the maximum value at 0.008 mol of citric acid. Above 0.007 mol of citric acid, it is obvious that the heat of combustion of $LaMn(C_6H_5O_7)(NO_3)_3$ increased with the amount of citric acid, so that D_{024} increased and the specific surface area decreased as shown in Table 1. Below 0.007 mol of citric acid, the heat of combustion of $LaMn(C_6H_5O_7)(NO_3)_3$ decreased due to the co-existence of $La(NO_3)_3 \cdot xH_2O$ and $Mn(NO_3)_2 \cdot xH_2O$, and
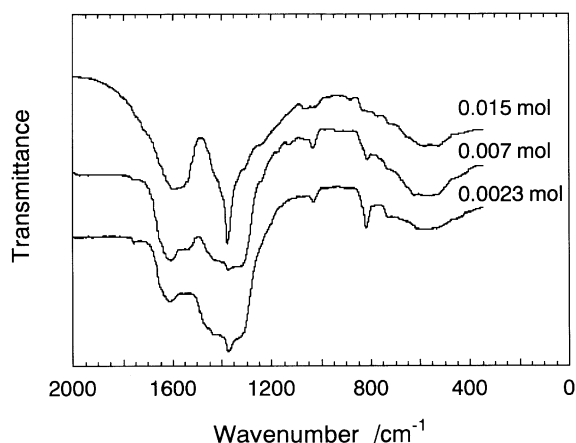

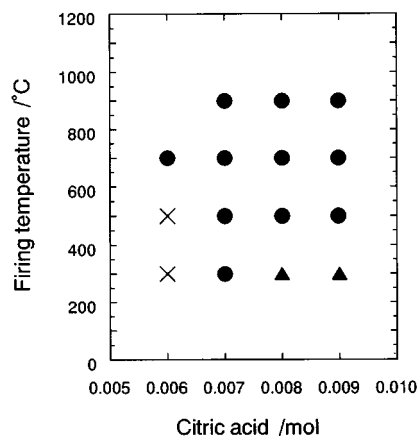FIG. 2. IR spectra of the gels with 0.0023, 0.007, and 0.015 mol of citric acid.

FIG. 3. Relationship between crystal structure of the samples and synthesis condition (amount of citric acid and firing temperature). (●) hexagonal $LaMnO_{3+\delta}$, (▲) mixture of hexagonal $LaMnO_{3+\delta}$ and La_2O_3, (×) amorphous

TABLE 1
Relationship between Oxygen Content (3+δ), Crystallite Size (D_{024}), Specific Surface Area (S) of LaMnO$_{3+\delta}$ and Synthesis Condition (Amount of Citric Acid and Firing Temperature)

Synthesis condition			D_{024}	S
Amount (mol)	Temp. (°C)	3 + δ	(nm)	(m^2/g)
0.006	500	—	—	—
0.007	500	3.23	12.2	16.3
0.008	500	3.20	14.8	18.5
0.009	500	3.17	18.4	15.2
0.006	700	3.19	21.5	12.9
0.007	700	3.20	16.4	14.2
0.008	700	3.18	20.2	15.7
0.009	700	3.19	22.4	13.1

FIG. 5. Relationship between specific surface area (S) and firing temperature of the gel with 0.007 mol of citric acid. Specific surface area (S) of LaMnO$_{3+\delta}$ synthesized using PAA and solid-state reaction is also plotted.

we could not obtain LaMnO$_{3+\delta}$ by firing the gel at 500°C. Since we could not observe the change in DTA and TG above 500°C, the increase of D_{024} at 700°C is considered to be caused by sintering of LaMnO$_{3+\delta}$. From the results of Table 1, we considered that LaMnO$_{3+\delta}$ firing the gel with 0.007–0.008 mol of citric acid had a very fine powder. Hereafter, we used the gel with 0.007 mol of citric acid to characterize the surface of LaMnO$_{3+\delta}$.

Figure 4 shows the relationship between D_{024} and the firing temperature of the gel with 0.007 mol of citric acid. In Fig. 4, we also plotted D_{024} calculated from LaMnO$_{3+\delta}$ synthesized using poly(acrylic) acid (PAA) and the solid-state reaction. D_{024} increases with temperature. At 900°C, D_{024} of LaMnO$_{3+\delta}$ synthesized using the solid-state reaction is less than D_{024} of LaMnO$_{3+\delta}$ synthesized using citric

acid and PAA. Figure 5 shows the relationship between the specific surface area and the firing temperature of the gel with 0.007 mol of citric acid. The specific surface area of LaMnO$_{3+\delta}$ synthesized using citric acid decreases from ≈ 16.7 (400°C) to ≈ 3.0 m^2/g (900°C). At low temperature, the specific surface area of LaMnO$_{3+\delta}$ synthesized using PAA is larger than the specific surface area of LaMnO$_{3+\delta}$ synthesized using citric acid.

The XPS spectra of the La3$d_{5/2}$, Mn2$p_{3/2}$, and O1s levels of LaMnO$_{3+\delta}$ synthesized using citric acid are shown in Figs. 6a, 6b, and 6c, respectively. A satellite peak was observed on the high binding energy side of the main La3$d_{5/2}$ peaks by ≈ 4 eV. This satellite was interpreted as the excitation of an electron from the anion valence band into the lanthanum f band (15). The Mn2$p_{3/2}$ level is broad, and asymmetric toward the high binding energy site. The binding energies of the La3$d_{5/2}$ and Mn2$p_{3/2}$ levels are shown in Table 2 and are independent of the synthesis condition: 834.3 $\pm$ 0.2 eV for the La3$d_{5/2}$ level and 642.0 $\pm$ 0.2 eV for the Mn2$p_{3/2}$ level, respectively. We could not observe the large variation in both the binding energies and FWHM of the La3$d_{5/2}$ and Mn2$p_{3/2}$ levels. The O1s level has two peaks, and these peaks are independent of the synthesis condition. The lower binding peak is $\approx 529.3 \pm 0.2$ eV and assignable to a lattice oxygen. The higher binding peak is $\approx 531.0 \pm 0.2$ eV and assignable to an adsorbed oxygen or hydroxyl group (16, 17). The La/Mn ratio of the LaMnO$_{3+\delta}$ surface is also shown in Table 2. Except for LaMnO$_{3+\delta}$ firing the gel with 0.007 mol of citric acid at 500°C, the La/Mn ratio is 1.2–1.3 and is independent of the synthesis condition.

The conversion from CO to CO$_2$ was measured for LaMnO$_{3+\delta}$ synthesized using citric acid and is shown in Fig. 7. The gel with 0.007 mol of citric acid was fired at
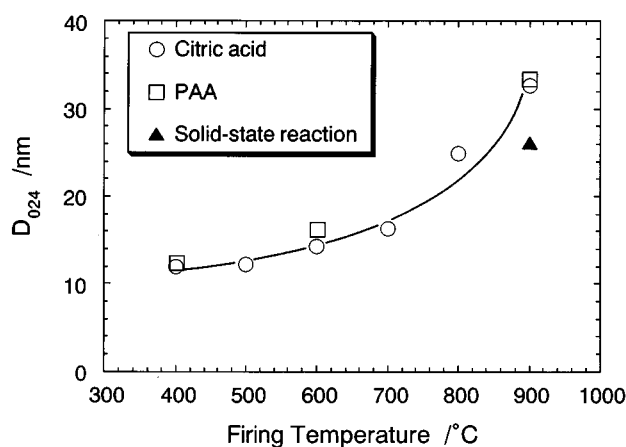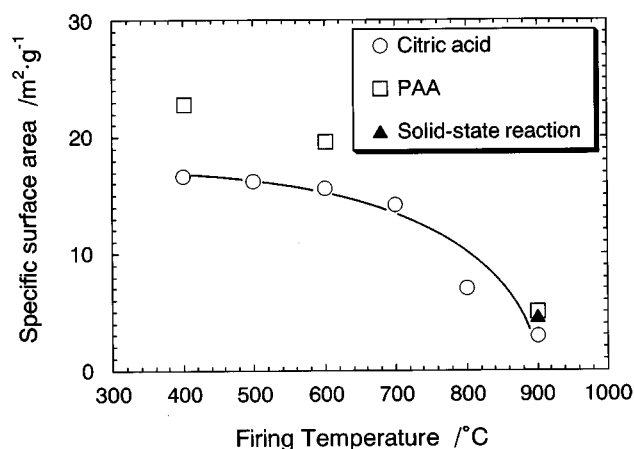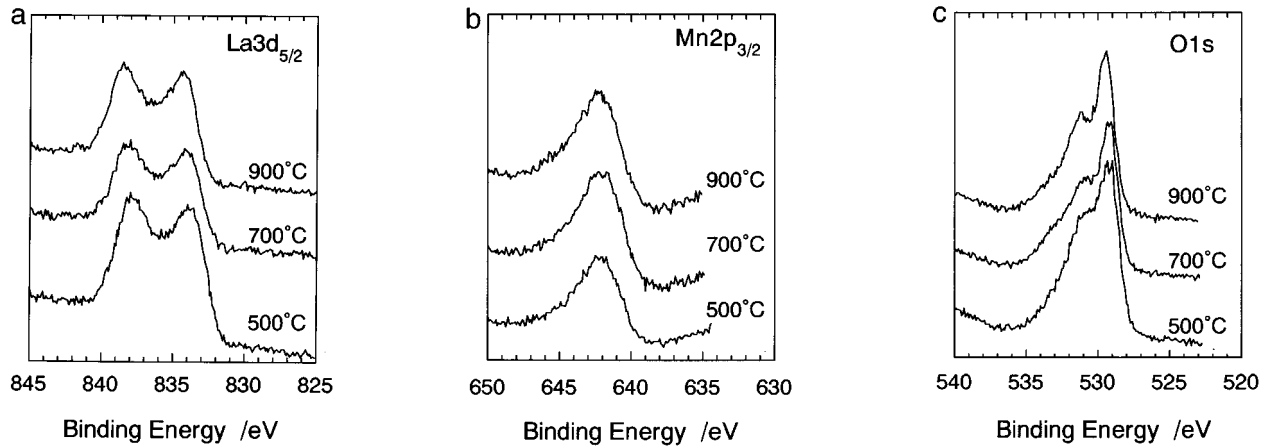

FIG. 4. Relationship between crystallite size (D_{024}) and firing temperature of the gel with 0.007 mol of citric acid. D_{024} of LaMnO$_{3+\delta}$ synthesized using PAA and solid-state reaction is also plotted.

FIG. 6. XPS spectra of the La3d$_{5/2}$, Mn2p$_{3/2}$, and O1s levels of LaMnO$_{3+\delta}$ firing the gels with 0.007 mol of citric acid.

400–900°C. The conversion increased in the firing temperature range from 400 to 600°C and had a maximum value, then decreased in the firing temperature range from 700 to 900°C. The rate of reaction (R) at a given temperature was calculated using the equation

$$R = \frac{F \times C \times C_v}{m \times S},$$

where F is the gas flow per minute, C the initial concentration of CO, C_v the conversion per gram from CO to CO$_2$, m the mass of the sample and S specific surface area of the sample (18). Figure 8 shows the relationship between the rate of reaction at 270°C and the firing temperatures of the gels. The rate of reaction for LaMnO$_{3+\delta}$ synthesized using PAA and the solid-state reaction is also plotted in Fig. 8. The rate of reaction for LaMnO$_{3+\delta}$ synthesized using citric

acid increased in the firing temperature range from 400 to 600°C, and had a constant value in the firing temperature range from 600 to 900°C. It is obvious that LaMnO$_{3+\delta}$ synthesized using citric acid has a large rate of reaction at low temperature. On firing at 900°C, the rate of reaction of LaMnO$_{3+\delta}$ synthesized using solid-state reaction is larger by ≈ 0.1 cm$^3 \cdot$min$^{-1} \cdot$m^{-2} than those of LaMnO$_{3+\delta}$ synthesized using citric acid and PAA. Since we cannot find the difference in the specific surface areas of LaMnO$_{3+\delta}$ synthesized using citric acid, PAA, and solid-state reaction, it is considered that the La/Mn ratio of LaMnO$_{3+\delta}$ synthesized using solid-state reaction is different from the La/Mn ratio of LaMnO$_{3+\delta}$ synthesized using citric acid and PAA.

Voorhoeve *et al.* reported that the oxidation of CO occurs at the metal ions of the surface (19). Both the metal ion content and the surface crystallinity (regularity of the ions)

TABLE 2
Relationship between Binding Energies of La3$d_{5/2}$ and Mn2$p_{3/2}$ Levels of LaMnO$_{3+\delta}$ and Synthesis Condition (Amount of Citric Acid and Firing Temperature)

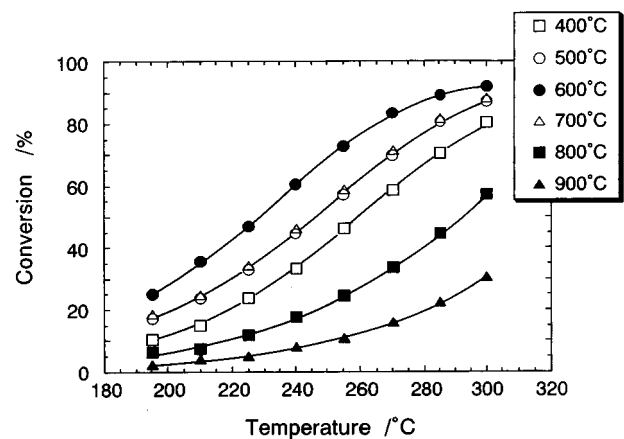| Synthesis condition		La3$d_{5/2}$ (eV)	FWHM (eV)	Mn2$p_{3/2}$ (eV)	FWHM (eV)	La/Ma
Amount (mol)	Temp. (°C)					
0.007	500	834.1	6.6	641.8	3.4	1.5
0.007	700	834.3	6.5	641.8	3.7	1.2
0.007	900	834.4	6.4	642.2	3.7	1.3
0.006	700	834.3	6.5	642.0	3.6	1.3
0.007	700	834.3	6.5	641.8	3.7	1.2
0.008	700	834.2	6.4	642.0	3.9	1.2

FIG. 7. Conversion from CO to CO$_2$ on LaMnO$_{3+\delta}$ firing the gels with citric acid.
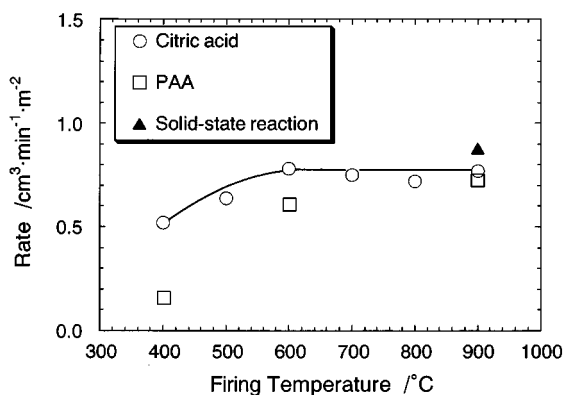
FIG. 8. Relationship between the rate of reaction (R) at 270°C and firing temperature of the gels with 0.007 mol of citric acid. The rate of LaMnO$_{3+\delta}$ synthesized using PAA and solid-state reaction is also plotted.

play an important role to the catalytic activity. As seen in Fig. 6c, it is obvious that there are two kinds of oxygen at the surface; one is lattice oxygen, and the other is oxygen adsorbed on the metal ions. CO$_2$ is produced by the reaction of CO with oxygen adsorbed on the metal ions of the outermost surface. After the desorption of CO$_2$ from the surface, oxygen is again adsorbed on the metal ions. In the present study, we can understand that the low rate of reaction for LaMnO$_{3+\delta}$ synthesized using citric acid below 600°C was caused by the deviation of the La/Mn ratio. Because of the rapid combustion of PAA, LaMnO$_{3+\delta}$ synthesized using PAA has many cracks, resulting in a larger specific surface area and insufficient crystallization (10). The large rate of reaction for LaMnO$_{3+\delta}$ synthesized using citric acid indicated that LaMnO$_{3+\delta}$ has sufficient crystallization and has many adsorption sites. From these results, citric acid is better than PAA for improving the crystallinity of the LaMnO$_{3+\delta}$ surface.

CONCLUSION

Thermal analysis and IR spectra indicate that the gel with 0.0023 mol of citric acid is a mixture of LaMn(C$_6$H$_5$O$_7$)(NO$_3$)$_3$, La(NO$_3$)$_3 \cdot x$H$_2$O, and Mn(NO$_3$)$_2 \cdot x$H$_2$O, the gel with 0.007 mol of citric acid is LaMn(C$_6$H$_5$O$_7$)(NO$_3$)$_3$, and the gel with 0.015 mol of citric acid is LaMn(C$_6$H$_5$O$_7$)$_2$. By firing the gel with 0.007 mol of

citric acid, hexagonal perovskite-type LaMnO$_{3+\delta}$ was obtained at 300–900°C. The catalytic activity for CO oxidation indicates that the rate of reaction for LaMnO$_{3+\delta}$ synthesized using citric acid is better than that for LaMnO$_{3+\delta}$ synthesized using PAA. It is considered that citric acid improves the crystallinity (regularity of the ions) of the LaMnO$_{3+\delta}$ surface.

ACKNOWLEDGMENT

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